Intramolecular cyclization of *O*-(3,5-dinitrophenyl) and *O*-(3-amino-5-nitrophenyl) ketoximes, products of transformations of 1,3,5-trinitrobenzene. The synthesis of nitrobenzo[*b*]furans and 4-hydroxynitroindoles

*S. S. Vorob´ev, M. D. Dutov, I. A. Vatsadze, E. P. Petrosyan, V. V. Kachala, Yu. A. Strelenko, and S. A. Shevelev**

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (495) 135 5328. E-mail: Shevelev@ioc.ac.ru

O-(3,5-Dinitrophenyl) ketoximes obtained in the reactions of ketoximes with 1,3,5-trinitrobenzene undergo acid-catalyzed cyclization into 2-substituted or 2,3-disubstituted 4,6-dinitrobenzo[*b*]furans. In analogous cyclization, products of selective reduction of a nitro group in *O*-(3,5-dinitrophenyl) ketoximes unexpectedly yield, along with 6-amino-4-nitrobenzofurans, 4-hydroxy-6-nitroindoles. The 4-NO_2 group is displaced from 4,6-dinitrobenzo[*b*]furans in reactions with thiols in the presence of K_2CO_3. Conditions for nitration and sulfochlorination of 4,6-dinitrobenzo[*b*]furans in position 3 were found. Condensation of a 2-methyl derivative with dimethylformamide acetal was accomplished.

Key words: 1,3,5-trinitrobenzene, (3,5-dinitrophenyl) ketoximes, *O*-(3-amino-5-nitrophenyl) ketoximes, 6-amino-4-nitrobenzofurans, 4-hydroxy-6-nitroindoles, 4,6-dinitrobenzofurans, nucleophilic displacement of nitro groups, cyclization.

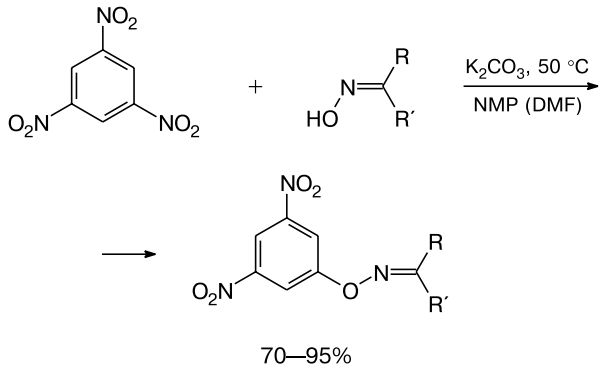
The present work was performed within the scope of investigations of 1,3,5-trinitrobenzene (TNB) for use as a multipurpose synthon, including the synthesis of polyfunctional benzoannulated heterocycles. These investigations are included in the program for chemical disposal of explosive 2,4,6-trinitrotoluene (TNT) and its conversion into a chemical raw material for various applications.[1,2] 1,3,5-Trinitrobenzene can be easily derived from TNT by two-step oxidative demethylation.[3,4]

A characteristic feature of TNB is its ability to add nucleophiles at the *ortho*-position relative to the nitro group to form stable anionic σ-H complexes.[5—8] Earlier,[9—14] we have found conditions for displacement of one or more nitro groups in TNB by a number of anionic O-, S-, and N-nucleophiles. The resulting products can serve as starting materials for the synthesis of new polyfunctional aromatic and heterocyclic structures.

Recently,[14] we have demonstrated that ketoximes and aldoximes in the presence of a base displace a nitro group from TNB to give earlier unknown *O*-(3,5-dinitrophenyl) oximes (Scheme 1).

Here we found that *O*-(3,5-dinitrophenyl) ketoximes **1** containing a methyl group (R^1 = H) or a methylene fragment (R^1 = Alk) at the C atom of the C=N bond smoothly undergo cyclization under mild conditions into 2-substituted (for R^1 = H) or 2,3-disubstituted (for R^1 = Alk) 4,6-dinitrobenzo[*b*]furans **2** (Scheme 2)*.

Scheme 1



70—95%

R, R´ = H, Alk, Ar, Het

NMP is *N*-methylpyrrolidone

Cyclization occurred even upon heating (>80 °C) of oximes **1** in *N*-methylpyrrolidone (NMP) or DMF; however, the best results were achieved under acid catalysis conditions: reflux in conc. HCl + ethanol (1 : 1 v/v) (for

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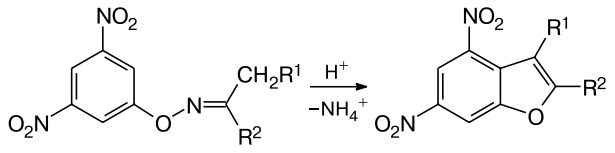
Scheme 2



1a—o **2a—o**

1, **2:** R^1 = H, R^2 = Me (**a**), Ph (**b**), 4-BrC_6H_4 (**c**), 4-FC_6H_4 (**d**), 3,4-methylenedioxyphenyl (**e**), 4-pyridyl (**f**), 2-pyridyl (**g**), 2-$MeOC_6H_4$ (**h**), 2,5-$(MeO)_2C_6H_3$ (**i**), 4-HOC_6H_4 (**j**), 2-furyl (**k**), 2-thienyl (**l**); R^1R^2 = —$(CH_2)_4$— (**m**), —$CH_2CH(Me)CH_2CH_2$— (**n**); R^1 = Me, R^2 = Ph (**o**)

1a—e,h—l), heating (80 °C) in conc. H_2SO_4 + AcOH (1 : 1 v/v) (for **1f,g** with formation of sulfates **2f,g** as products), or reflux in conc. HCl + AcOH (2 : 5 v/v) (for **1m—o**). The reaction was carried out until the starting oxime was consumed completely (4—18 h). The yields of 4,6-dinitrobenzo[*b*]furans **2** were 60—95%.

The proposed approach is a new and general route to 2-substituted and 2,3-disubstituted 4,6-dinitrobenzo[*b*]furans. The described[16,17] synthesis of 2-substituted 3-acyl-4,6-dinitrobenzo[*b*]furans involves intramolecular cyclization of *C*-picrylated 1,3-dicarbonyl compounds. The synthesis of some 2-substituted 4,6-dinitrobenzo[*b*]furans is of particular character.[18—20]

It should be noted that acid-catalyzed intramolecular cyclization of *O*-aryl oximes into benzofurans is well known[21—27] and analogous to the Fischer transformation of *N*-arylhydrazones into indoles.[28] The mechanism proposed[25,26] for this cyclization is shown in Scheme 3.

According to modern concepts,[26] the key step of the reaction is an acid-catalyzed [3,3]-sigmatropic rearrangement of the enehydroxylamine form of *O*-aryl oxime (**B** → **C**) followed by aromatization of the six-membered ring (**C** → **D**), closure of a dihydrofuran ring (**D** → **E**), and its aromatization *via* elimination of the ammonium ion (**E** → **F**). Based on this mechanism and generalized literature data, Guzzo *et al.*[26] have concluded that [3,3]-sigmatropic rearrangement should be favored by electron-donating substituents in the benzene ring but hindered by electron-withdrawing ones. Although cyclization of *O*-aryl oximes containing strong electron-withdrawing groups in the aryl fragment has been described,[22,24] all documented examples involve very drastic conditions with electron-withdrawing groups (NO_2, CN, RSO_2, *etc.*) being *meta* to the C atom at which ring closure occurs; if two such groups are present simultaneously, the yield of the resulting benzofuran is substantially lower.[22,24]

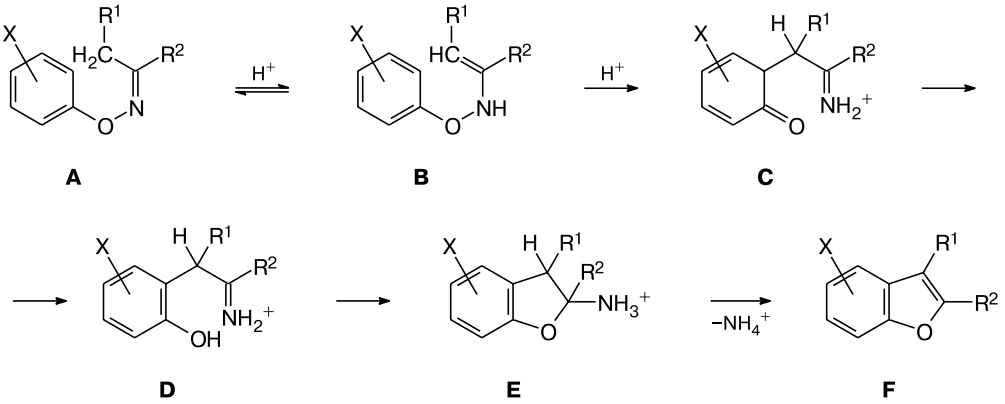
In the present work, we were the first to carry out cyclization of *O*-aryl oximes into products with a new C—C bond formed at the C atom that is *ortho*/*para* to strong electron-withdrawing substituents (two nitro groups). Apparently, this arrangement of electron-withdrawing substituents is more favorable for cyclization of *O*-aryl oximes than their *meta*-position relative to a new C—C bond.

We made a preliminary estimation of the reactivities of 4,6-dinitrobenzo[*b*]furans **2** in a number of standard reactions.

We studied the possibility of and conditions for nucleophilic displacement of a nitro group in 4,6-dinitrobenzo[*b*]furans **2**. As expected, dinitrobenzofurans **2** are not highly electrophilic because of the π-abundant character of the benzofuran system, which can hinder nucleophilic displacement of a nitro group. Nevertheless, we found conditions in which a nitro group (4-NO_2) that is in *peri*-position is displaced in reactions with aromatic and aliphatic thiols in NMP in the presence of K_2CO_3 as a deprotonating agent. This can be suitable for the synthesis of novel 4-RS-6-nitrobenzo[*b*]furans **3** (Scheme 4).

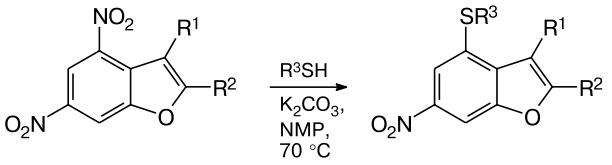
Displacement of the 4-NO_2 group in dinitrobenzofurans **2** was proven by NOE data for 4-(4-chlorophenylthio)-3-methyl-6-nitro-2-phenylbenzo[*b*]furan (**3i**) as an example. The NOE experiment revealed a coupling between the H(5) proton of the nitrobenzene ring and the H(2′) and H(6′) protons of the thiol substituent and cou-

Scheme 3



A **B** **C** **D** **E** **F**

Scheme 4



2a,b,o **3a—i**

3	R^1	R^2	R^3	**3**	R^1	R^2	R^3
a	H	Me	Ph	**f**	Me	Ph	$PhCH_2$
b	H	Ph	Ph	**g**	H	Me	$4\text{-}ClC_6H_4$
c	Me	Ph	Ph	**h**	H	Ph	$4\text{-}ClC_6H_4$
d	H	Me	$PhCH_2$	**i**	Me	Ph	$4\text{-}ClC_6H_4$
e	H	Ph	$PhCH_2$				

plings between the methyl protons in position 3 and the H(3´) and H(5´) protons of the thiol substituent. In the other cases, the RS fragment was located by comparing the ^{1}H NMR spectra. The displacement of only one nitro group was confirmed by the ^{1}H NMR spectra of the crude reaction product.

However, other anionic nucleophiles (phenols and fluorinated alcohols in the presence of bases, as well as NaN_3) are unable to displace an NO_2 group from dinitrobenzofurans **2**: no displacement occurred in NMP or DMF below 100 °C, while at higher temperatures, dinitrobenzofurans **2** decomposed. In this respect, dinitrobenzofurans differ substantially from 4,6-dinitrobenzo[*b*]thiophenes, which react under mild conditions not only with thiols but also with other anionic nucleophiles to give products of displacement of the 4-NO_2 group.[29,30] Apparently, the π-abundance of the benzo[*b*]furan system under study is much higher than that of the benzo[*b*]thiophene analog.

With 2-methyl-4,6-dinitrobenzo[*b*]furan (**2a**) as an example, we studied the reactivities of dinitrobenzofurans in electrophilic displacement reactions. It was found that compound **2a** is smoothly nitrated with H_2SO_4 + HNO_3 at position 3 to produce trinitro derivative **4** (Scheme 5).

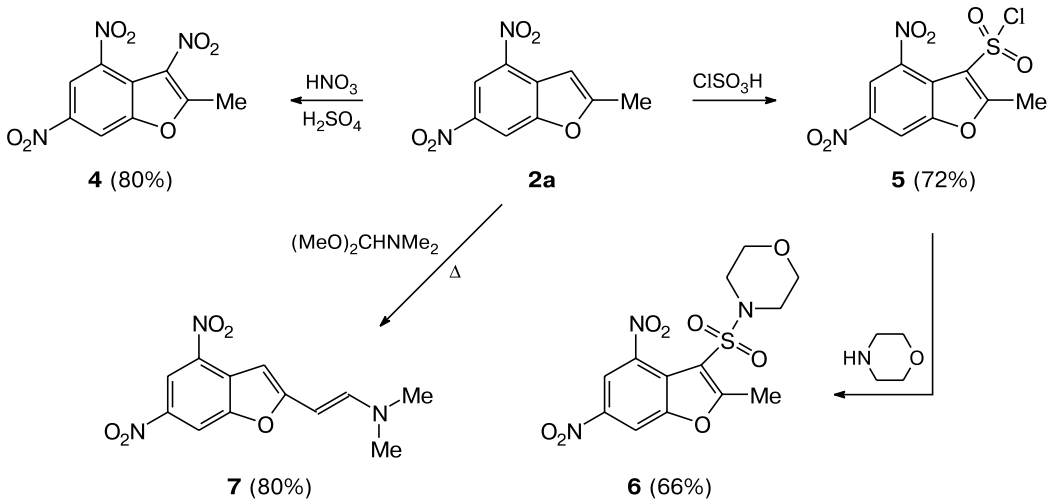
Dinitrobenzo[*b*]furan **2a** also readily undergoes sulfochlorination. The resulting sulfonyl chloride **5** reacts with morpholine to give the corresponding substituted sulfonamide **6** (see Scheme 5). At the same time, dinitrobenzofuran **2a** is inert to weaker electrophiles. For instance, its furan fragment cannot be formylated in the Vilsmeier reaction (heating with DMF—$SOCl_2$ or DMF—$POCl_3$) at free position 3, which is probably due to the deactivating effect of the nitro groups on electrophilic displacement.

The nitro groups increase the reactivity of the methyl group in the furan fragment: 2-methyl-4,6-dinitrobenzo[*b*]furan (**2a**) can enter into reactions characteristic of an activated methyl group. For example, heating of compound **2a** with dimethylformamide dimethyl acetal gave the corresponding enamine **7** (see Scheme 5), which is a suitable precursor of various polyfunctional derivatives.[31]

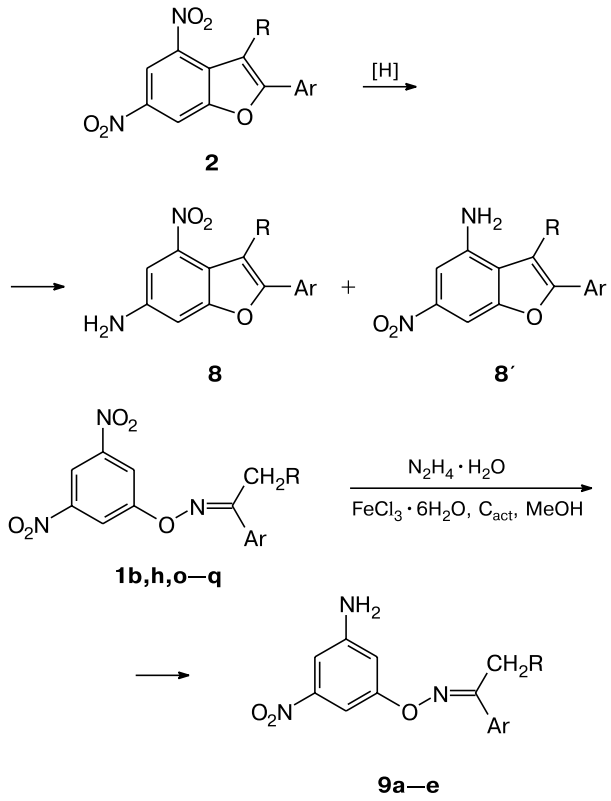
An important approach to functionalization of dinitrobenzofurans **2** could involve their reduction to aminonitrobenzo[*b*]furans followed by various transformations of the amino group yielding new nitrobenzofurans.

When we used standard systems for reduction of an aromatic nitro group ($NH_2NH_2 \cdot H_2O$ + catalysts, Fe in an acidic medium, and $SnCl_2$) in amounts required to reduce only one group, the reduction of dinitrobenzofurans **2** proceeded nonselectively to give a difficult-to-separate mixture of aminonitrobenzofurans **8** and **8´** in all cases (^{1}H NMR data) (Scheme 6). For this reason, we followed an alternative route to aminonitrobenzofurans, namely, acid-catalyzed cyclization of *O*-(3-amino-5-nitrophenyl) ketoximes obtained by reduction of one nitro group in *O*-(3,5-dinitrophenyl) ketoximes **1**.

Scheme 5



Scheme 6

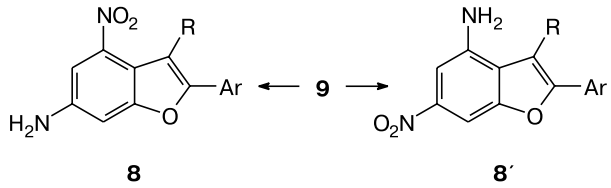


R = H, Ar = Ph (**1b**, **9a**); R = H, Ar = 4-ClC_6H_4 (**1p**, **9b**); R = H, Ar = 2-ClC_6H_4 (**1q**, **9c**); R = H, Ar = 2-$MeOC_6H_4$ (**1h**, **9d**); R = Me, Ar = Ph (**1o**, **9e**)

Selective reduction of *O*-(3,5-dinitrophenyl) ketoximes **1** with hydrazine hydrate in the presence of $FeCl_3$ and activated carbon proceeded smoothly to give *O*-(3-amino-5-nitrophenyl) ketoximes **9** (see Scheme 6).

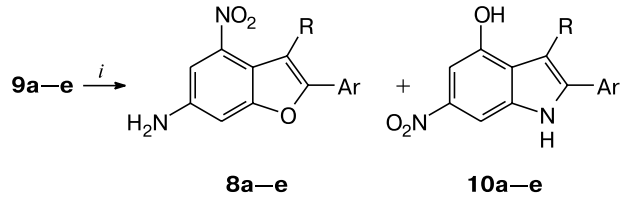
It is worth noting that cyclization of ketoximes **9** can occur in different ways: at the C atom that is *ortho* to the NO_2 group or at the C atom adjacent to the NH_2 group; the resulting products are 6-amino-4-nitro- (**8**) or 4-amino-6-nitrobenzo[*b*]furans (**8′**), respectively (Scheme 7).

Scheme 7



We found that heating of *O*-(3-amino-5-nitrophenyl) ketoximes **9** in a mixture of conc. HCl (36%) and ethanol (1 : 1, v/v) always gives a ~1 : 1 mixture of two products with the same elemental composition; their mass spectra contain equal (in mass) peaks of molecular ions with different patterns of fragmentation. The mixture was separated because the products are differently soluble in the reaction mixture (the total yields were 55—70%). We identified one product as substituted 6-amino-4-nitrobenzo[*b*]furan **8** (Scheme 8) and confirmed its structure by ^{1}H NMR spectroscopy: the NOE experiment revealed a coupling between the NH_2 protons and the H(5) and H(7) protons of the nitrobenzene ring. Unexpectedly, the other product was identified as substituted 4-hydroxy-6-nitroindole **10** (see Scheme 8): its ^{1}H NMR spectrum shows characteristic signals for the NH group of the indole ring (δ 12.15) and for the OH group of the nitrobenzene ring (δ 10.4). The NOE experiment revealed couplings between the OH proton and the H(5) proton of the nitrobenzene fragment and between the NH proton in the indole ring and the H(7) proton of the nitrobenzene fragment. The presence of an OH group was also proved chemically: indoles **10** are highly soluble in dilute aqueous alkali (indoles even with two nitro groups in the benzene ring[32] were found to be insoluble in dilute aqueous alkali at ambient temperature)*.

Scheme 8



i. HCl (conc.), EtOH, Δ.

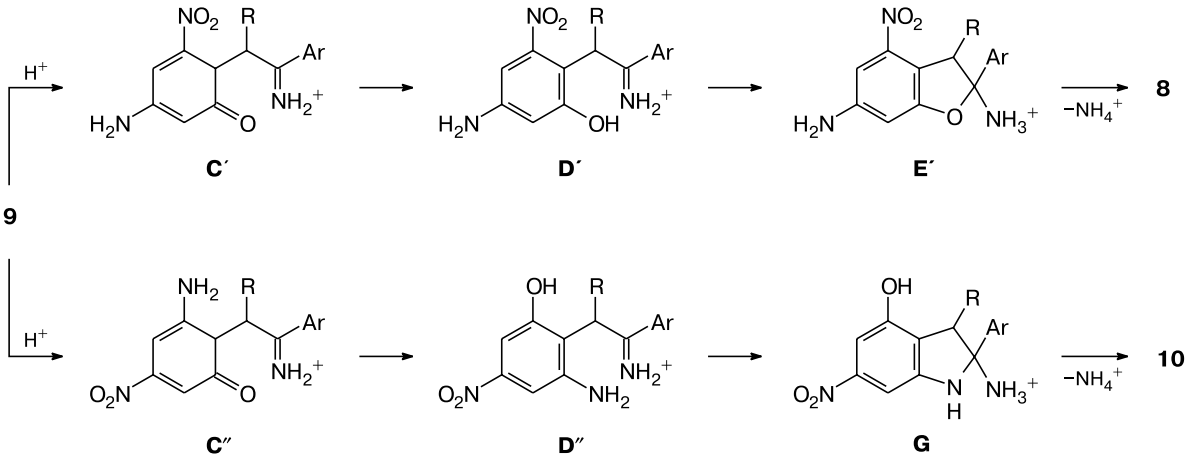
R = H, Ar = Ph (**a**); R = H, Ar = 4-ClC_6H_4 (**b**); R = H, Ar = 2-ClC_6H_4 (**c**); R = H, Ar = 2-$MeOC_6H_4$ (**d**); R = Me, Ar = Ph (**e**)

This unexpected outcome can be explained in terms of the generally accepted mechanism of cyclization of *O*-aryl ketoximes into benzo[*b*]furans[26] (see Scheme 3). As noted above, the key step of this transformation is an acid-catalyzed [3,3]-sigmatropic rearrangement of the enehydroxylamine form of *O*-aryl oxime (**B** → **C**) followed by aromatization of the six-membered ring (**C** → **D**), intramolecular addition of the OH group to the C=NH_2^+ bond (**D** → **E**), and elimination of the ammonium ion, leading to benzo[*b*]furan (**E** → **F**) (see Scheme 3).

According to the data obtained, [3,3]-sigmatropic rearrangement (**B** → **C**) of *O*-(3-amino-5-nitrophenyl) ketoximes **9** is equally probable at the *ortho*-position with respect to both the NO_2 and NH_2 groups, giving intermediates **C′** and **C″** and then **D′** and **D″**, respectively (Scheme 9). Intermediates **D′** undergo usual cyclization into 6-amino-4-nitrobenzo[*b*]furans **8** (see Scheme 9, **D′** → **E′** → **8**). In the case of intermediates **D″**, the

* For the preliminary communication, see Ref. 33.

Scheme 9



intramolecular addition to the $C{=}NH_2^+$ bond probably involves the NH_2 group (**D″** → **G**) rather than the OH group and subsequent elimination of the ammonium ion produces 4-hydroxy-6-nitroindoles **10** (see Scheme 9, **G** → **10**). Here the nonionized OH group cannot compete with the much more nucleophilic NH_2 group; otherwise, we would obtain 4-amino-6-nitrobenzofurans **8´**, which is not the case.

Analogous results were obtained when cyclization was carried out in other acid mixtures (MeOH—HCl (conc.), reflux; MeOH—HCl (gas), reflux; CF_3COOH, reflux; AcONa—AcOH, 80 °C; AcOH—H_2SO_4, 60 °C; H_2SO_4, 60 °C; $POCl_3$—benzene, reflux) and a Lewis acid ($ZnCl_2$—*p*-cresol, 180 °C). In all the cases, the ratio **8** : **10** was ~1 : 1. Cyclization of ketoximes with the protected amino group (*O*-(3-acetylamino-5-nitrophenyl) and *O*-(5-nitro-3-phthalimidophenyl) ketoximes)—in order to make the reaction follow the pathway leading to aminonitrobenzofuran **8´**—gave, as with *O*-(3-amino-5-nitrophenyl) ketoximes, a ~1 : 1 mixture of compounds **8** and **10**; *i.e.*, the protective group is eliminated under the reaction conditions before cyclization.

Thus, we discovered that *O*-aryl ketoximes containing a *meta*-amino group in the aryl fragment undergo intramolecular cyclization into 4-hydroxyindoles rather than benzo[*b*]furans as always reported for this cyclization.

Experimental

^{1}H NMR spectra were recorded on a Bruker AC-250 spectrometer. Mass spectra (EI) were recorded on a Kratos MS-30 instrument (the spectra of all compounds showed a molecular ion peak $[M]^+$). The course of the reaction was monitored by TLC on Silufol UV-254 plates.

O-(3,5-Dinitrophenyl) ketoximes **1a—q** were prepared according to a known procedure.[14]

Synthesis of 4,6-dinitrobenzo[*b*]furans 2a—o (general procedure). Appropriate *O*-(3,5-dinitrophenyl) ketoxime **1** (0.01 mol) was added to a mixture of ethanol (10 mL) and 36% HCl (10 mL) (for **1m—o**, AcOH (10 mL) + conc. HCl (4 mL); for **1f,g**, conc. H_2SO_4 (5 mL) + AcOH (5 mL), the target products being obtained as sulfates). The reaction mixture was refluxed (for **1f,g**, heating at 80 °C) until the starting dinitro compound was completely consumed (monitoring by TLC with $CHCl_3$ as an eluent). On cooling to ~20 °C, the precipitate that formed was filtered off, recrystallized from acetonitrile, and dried *in vacuo* (for **2f,g**, the reaction mixture was poured into water, the resulting sulfate of **2f** or **2g** was filtered off, washed with water, dried in air, and recrystallized from acetonitrile).

2-Methyl-4,6-dinitrobenzo[*b*]furan (2a). Reaction time 6 h, yield 93%, m.p. 143—144 °C. Found (%): C, 48.42; H, 2.91; N, 12.23. $C_9H_6N_2O_5$. Calculated (%): C, 48.66; H, 2.72; N, 12.61. ^{1}H NMR (DMSO-d_6), δ: 2.65 (s, 3 H); 7.32 (s, 1 H); 8.78, 8.90 (both d, 1 H each, ^4J = 1.9 Hz).

4,6-Dinitro-2-phenylbenzo[*b*]furan (2b). Reaction time 18 h, yield 95%, m.p. 178—179 °C. Found (%): C, 59.42; H, 2.52; N, 9.47. $C_{14}H_8N_2O_5$. Calculated (%): C, 59.16; H, 2.84; N, 9.86. ^{1}H NMR (DMSO-d_6), δ: 7.57, 8.15 (both m, 3 H each); 8.82, 8.97 (both d, 1 H each, ^4J = 2.0 Hz).

2-(4-Bromophenyl)-4,6-dinitrobenzo[*b*]furan (2c). Reaction time 7 h, yield 77%, m.p. 248—249 °C. Found (%): C, 45.98; H, 1.63; N, 7.92. $C_{14}H_7BrN_2O_5$. Calculated (%): C, 46.31; H, 1.94; N, 7.71. ^{1}H NMR (DMSO-d_6), δ: 7.75, 8.07 (both d, 2 H each, ^3J = 8.0 Hz); 8.17 (s, 1 H); 8.85, 8.97 (both d, 1 H each, ^4J = 2.0 Hz).

2-(4-Fluorophenyl)-4,6-dinitrobenzo[*b*]furan (2d). Reaction time 6 h, yield 92%, m.p. 214—215 °C. Found (%): C, 55.87; H, 2.11; N, 9.52. $C_{14}H_7FN_2O_5$. Calculated (%): C, 55.64; H, 2.33; N, 9.27. ^{1}H NMR (DMSO-d_6), δ: 7.40 (t, 2 H, ^3J = 7.8 Hz); 8.05 (s, 1 H); 8.17 (t, 2 H, ^3J = 7.8 Hz); 8.80, 8.95 (both d, 1 H each, ^4J = 2.1 Hz).

2-(3,4-Methylenedioxyphenyl)-4,6-dinitrobenzo[*b*]furan (2e). Reaction time 4 h, yield 86%, m.p. 268—269 °C. Found (%): C, 56.01; H, 3.11; N, 8.22. $C_{16}H_{10}N_2O_7$. Calculated (%): C, 56.15; H, 2.94; N, 8.18. ^{1}H NMR (DMSO-d_6), δ: 6.15 (s, 2 H); 7.10 (d, 1 H); 7.61 (s, 2 H); 7.95 (s, 1 H); 8.82, 8.87 (both d, 1 H each, ^4J = 2.0 Hz).

4,6-Dinitro-2-(4-pyridyl)benzo[*b*]furan (2f). Reaction time 3 h, yield 88% (as sulfate), m.p. 162—163 °C. Found (%):

C, 41.01; H, 2.12; N, 10.43; S, 8.54. $C_{13}H_9N_3O_9S$. Calculated (%): C, 40.74; H, 2.37; N, 10.96; S, 8.37. ^{1}H NMR (DMSO-d_6), δ: 8.03 (d, 2 H, ^3J = 8.0 Hz); 8.40 (s, 1 H); 8.79 (d, 2 H, ^3J = 8.0 Hz); 8.85, 9.07 (both d, 1 H each, ^4J = 2.0 Hz).

4,6-Dinitro-2-(2-pyridyl)benzo[*b*]furan (2g). Reaction time 10 h, yield 72% (as sulfate), m.p. 174—175 °C. Found (%): C, 41.12; H, 2.68; N, 11.32; S, 8.77. $C_{13}H_9N_3O_9S$. Calculated (%): C, 40.74; H, 2.37; N, 10.96; S, 8.37. ^{1}H NMR (DMSO-d_6), δ: 7.53 (t, 1 H, ^3J = 8.0 Hz); 8.10 (m, 3 H); 8.75 (m, 1 H); 8.83, 9.02 (both d, 1 H each, ^4J = 1.9 Hz).

2-(2-Methoxyphenyl)-4,6-dinitrobenzo[*b*]furan (2h). Reaction time 8 h, yield 80%, m.p. 227—228 °C. Found (%): C, 57.12; H, 3.27; N, 9.25. $C_{15}H_{10}N_2O_6$. Calculated (%): C, 57.33; H, 3.21; N, 8.91. ^{1}H NMR (DMSO-d_6), δ: 4.10 (s, 3 H); 7.21 (t, 1 H, ^3J = 7.8 Hz); 7.32 (d, 1 H, ^3J = 8.0 Hz); 7.58 (t, 1 H, ^3J = 8.0 Hz); 7.90 (s, 1 H); 8.05 (d, 1 H, J = 7.0 Hz); 8.82, 8.95 (both d, 1 H each, ^4J = 2.0 Hz).

2-(2,5-Dimethoxyphenyl)-4,6-dinitrobenzo[*b*]furan (2i). Reaction time 8 h, yield 84%, m.p. 252—253 °C. Found (%): C, 56.04; H, 3.21; N, 8.45. $C_{16}H_{12}N_2O_7$. Calculated (%): C, 55.82; H, 3.51; N, 8.14. ^{1}H NMR (DMSO-d_6), δ: 3.85, 4.07 (both s, 3 H each); 7.25 (d, 2 H, ^3J = 8.0 Hz); 7.51, 7.93 (both s, 1 H each); 8.83, 9.02 (both d, 1 H each, ^4J = 1.9 Hz).

2-(4-Hydroxyphenyl)-4,6-dinitrobenzo[*b*]furan (2j). Reaction time 12 h, yield 58%, m.p. 271—272 °C. Found (%): C, 56.35; H, 2.61; N, 9.81. $C_{14}H_8N_2O_6$. Calculated (%): C, 56.01; H, 2.69; N, 9.33. ^{1}H NMR (DMSO-d_6), δ: 6.95 (d, 2 H, ^3J = 8.0 Hz); 7.81 (s, 1 H); 7.93 (d, 2 H, ^3J = 8.0 Hz); 8.80, 8.84 (both d, 1 H each, ^4J = 2.0 Hz); 10.30 (s, 1 H).

2-(2-Furyl)-4,6-dinitrobenzo[*b*]furan (2k). Reaction time 5 h, yield 75%, m.p. 160—161 °C. Found (%): C, 52.33; H, 2.01; N, 10.66. $C_{12}H_6N_2O_6$. Calculated (%): C, 52.57; H, 2.21; N, 10.22. ^{1}H NMR (DMSO-d_6), δ: 6.84 (m, 1 H); 7.48 (d, 1 H, J = 5.0 Hz); 7.77, 8.09 (both s, 1 H each); 8.87, 8.98 (both d, 1 H each, ^4J = 1.9 Hz).

4,6-Dinitro-2-(2-thienyl)benzo[*b*]furan (2l). Reaction time 6 h, yield 80%, m.p. 165—166 °C. Found (%): C, 50.35; H, 2.18; N, 9.21. $C_{12}H_6N_2O_5S$. Calculated (%): C, 49.66; H, 2.08; N, 9.65. ^{1}H NMR (DMSO-d_6), δ: 7.24 (t, 1 H, J = 4.0 Hz); 7.72 (s, 1 H); 7.92 (m, 2 H); 8.71, 8.80 (both d, 1 H each, ^4J = 1.9 Hz).

7,9-Dinitro-1,2,3,4-tetrahydrodibenzofuran (2m). Reaction time 6 h, yield 85%, m.p. 102 °C. Found (%): C, 55.21; H, 4.01; N, 10.25. $C_{12}H_{10}N_2O_5$. Calculated (%): C, 54.97; H, 3.84; N, 10.68. ^{1}H NMR (DMSO-d_6), δ: 1.89, 2.84 (both m, 4 H each); 8.70, 8.85 (both d, 1 H each, ^4J = 2.0 Hz).

3-Methyl-7,9-dinitro-1,2,3,4-tetrahydrodibenzofuran (2n). Reaction time 9 h, yield 71%, m.p. 88 °C. Found (%): C, 56.68; H, 4.11; N, 10.05. $C_{13}H_{12}N_2O_5$. Calculated (%): C, 56.52; H, 4.38; N, 10.14. ^{1}H NMR (DMSO-d_6), δ: 1.10 (d, 3 H); 1.50 (m, 1 H); 1.95 (m, 2 H); 2.35 (m, 1 H); 2.90 (m, 3 H); 8.62, 8.75 (both d, 1 H each, ^4J = 2.0 Hz).

3-Methyl-4,6-dinitro-2-phenylbenzo[*b*]furan (2o). Reaction time 6 h, yield 73%, m.p. 151—152 °C. Found (%): C, 60.59; H, 3.56; N, 9.01. $C_{15}H_{10}N_2O_5$. Calculated (%): C, 60.41; H, 3.38; N, 9.39. ^{1}H NMR (DMSO-d_6), δ: 2.42 (s, 3 H); 7.62 (m, 3 H); 7.85 (m, 2 H); 8.70, 8.85 (both d, 1 H each, ^4J = 2.0 Hz).

Synthesis of 4-SR-6-nitrobenzo[*b*]furans 3a—i (general procedure). An appropriate thiol (1.5 mmol) was added under nitrogen to a stirred mixture of dinitrobenzofuran **2** (1 mmol) and K_2CO_3 (0.207 g, 1.5 mmol) in NMP (10 mL). The reaction mixture was stirred at 70 °C until the dinitro compound was completely consumed (monitoring by TLC with $CHCl_3$ as an eluent) and poured into ice water (50 mL). The precipitate that formed was filtered off and washed with water (2×10 mL). For products **3a,b,d,e,g**, the precipitate was dissolved in chloroform (25 mL) and filtered through a short column with silica gel (for **3i**, the volume of chloroform was 30 mL). The solution was twice washed with water and the organic layer was separated, dried over $MgSO_4$, and evaporated to dryness. The precipitate was recrystallized from glacial acetic acid.

2-Methyl-6-nitro-4-(phenylthio)benzo[*b*]furan (3a). Reaction time 2 h, yield 26%, m.p. 160—162 °C. Found (%): C, 63.01; H, 4.01; N, 4.78. $C_{15}H_{11}NO_3S$. Calculated (%): C, 63.14; H, 3.89; N, 4.91. ^{1}H NMR (DMSO-d_6), δ: 2.52 (s, 3 H); 6.55 (s, 1 H); 7.55—7.25 (m, 5 H); 8.85, 9.10 (both s, 1 H each).

6-Nitro-2-phenyl-4-(phenylthio)benzo[*b*]furan (3b). Reaction time 4 h, yield 29%, m.p. 110—112 °C. Found (%): 69.01; H, 3.91; N, 3.92. $C_{20}H_{13}NO_3S$. Calculated (%): C, 69.15; H, 3.77; N, 4.03. ^{1}H NMR (DMSO-d_6), δ: 7.40—8.65 (m, 9 H); 7.75 (s, 1 H); 8.95—7.95 (m, 2 H); 8.41 (s, 1 H).

3-Methyl-6-nitro-2-phenyl-4-(phenylthio)benzo[*b*]furan (3c). Reaction time 3.5 h, yield 41%, m.p. 147—149 °C. Found (%): C, 69.47; H, 4.31; N, 4.05. $C_{21}H_{15}NO_3S$. Calculated (%): C, 69.79; H, 4.18; N, 3.88. ^{1}H NMR (DMSO-d_6), δ: 2.62 (s, 3 H); 7.40—7.65 (m, 8 H); 7.72 (s, 1 H); 7.80—7.85 (m, 2 H); 8.41 (s, 1 H).

4-(Benzylthio)-2-methyl-6-nitrobenzo[*b*]furan (3d). Reaction time 2 h, yield 35%, m.p. 80—82 °C. Found (%): C, 64.01; H, 4.57; N, 4.34. $C_{16}H_{13}NO_3S$. Calculated (%): C, 64.20; H, 4.38; N, 4.68. ^{1}H NMR (DMSO-d_6), δ: 2.55 (s, 3 H); 4.45 (s, 2 H); 6.80 (m, 1 H); 7.21—7.43 (m, 5 H); 8.00, 8.30 (both s, 1 H each).

4-(Benzylthio)-6-nitro-2-phenylbenzo[*b*]furan (3e). Reaction time 8 h, yield 57%, m.p. 111—124 °C. Found (%): C, 69.97; H, 4.45; N, 3.54. $C_{21}H_{15}NO_3S$. Calculated (%): C, 69.79; H, 4.18; N, 3.88. ^{1}H NMR (DMSO-d_6), δ: 4.48 (s, 2 H); 7.20—7.62 (m, 9 H); 7.92—8.50 (m, 3 H); 8.32 (s, 1 H).

4-(Benzylthio)-3-methyl-6-nitro-2-phenylbenzo[*b*]furan (3f). Reaction time 3.2 h, yield 80%, m.p. 122—124 °C. Found (%): C, 70.00; H, 4.65; N, 3.94. $C_{22}H_{17}NO_3S$. Calculated (%): C, 70.38; H, 4.56; N, 3.73. ^{1}H NMR (DMSO-d_6), δ: 2.62 (s, 3 H); 4.45 (s, 2 H); 7.25—7.80 (m, 10 H); 7.96, 8.27 (both s, 1 H each).

4-(4-Chlorophenylthio)-2-methyl-6-nitrobenzo[*b*]furan (3g). Reaction time 2 h, yield 17%, m.p. 146—148 °C. Found (%): C, 56.47; H, 3.25; N, 4.68. $C_{15}H_{10}ClNO_3S$. Calculated (%): C, 56.34; H, 3.15; N, 4.38. ^{1}H NMR (DMSO-d_6), δ: 2.67 (s, 3 H); 6.61 (m, 1 H); 7.31—7.60 (m, 4 H); 8.85, 9.10 (both s, 1 H each).

4-(4-Chlorophenylthio)-6-nitro-2-phenylbenzo[*b*]furan (3h). Reaction time 4 h, yield 39%, m.p. 187—188 °C. Found (%): C, 63.09; H, 3.04; N, 3.81. $C_{20}H_{12}ClNO_3S$. Calculated (%): C, 62.91; H, 3.17; N, 3.67. ^{1}H NMR (DMSO-d_6), δ: 7.45—7.61 (m, 8 H); 7.92 (s, 1 H); 8.00—8.05 (m, 2 H); 8.50 (s, 1 H).

4-(4-Chlorophenylthio)-3-methyl-6-nitro-2-phenylbenzo[*b*]furan (3i). Reaction time 4.5 h, yield 30%, m.p. 137—139 °C. Found (%): C, 63.45; H, 3.34; N, 3.24. $C_{21}H_{14}ClNO_3S$. Calculated (%): C, 63.72; H, 3.56; N, 3.54. ^{1}H NMR (DMSO-d_6), δ: 2.60 (s, 3 H); 7.40—7.65 (m, 7 H); 7.80—7.86 (m, 2 H); 7.82, 8.50 (both s, 1 H each).

2-Methyl-3,4,6-trinitrobenzo[*b*]furan (4). 2-Methyl-4,6-dinitrobenzo[*b*]furan (**2a**) (2.22 g, 0.01 mol) was added at 10 °C to a vigorously stirred mixture of fuming HNO_3 (0.5 mL) and H_2SO_4 (4.5 mL). After 20 min, the reaction mixture was poured into ice water (50 mL) and the resulting precipitate was filtered off, washed with water (2×10 mL), and dried in air. The yield was 79%, m.p. 150—152 °C. Found (%): C, 40.21; H, 1.95; N, 15.95. $C_9H_5N_3O_7$. Calculated (%): C, 40.46; H, 1.89; N, 15.73. ^{1}H NMR ($CDCl_3$), δ: 2.95 (s, 3 H); 8.64, 8.85 (both s, 1 H each).

3-Chlorosulfonyl-2-methyl-4,6-dinitrobenzo[*b*]furan (5). 2-Methyl-4,6-dinitrobenzo[*b*]furan (**2a**) (1 g, 4.5 mmol) was added at 6 °C to $ClSO_3H$ (30 mmol, 6 mL). The reaction mixture was allowed to warm to ~20 °C, kept for an additional 40 min, and poured onto ice (50 mL). The resulting precipitate was filtered off, washed with water to neutral reaction, and dried in air. The yield was 72%, m.p. 198—200 °C. Found (%): C, 33.45; H, 1.57; Cl, 11.21; N, 8.21; S, 10.32. $C_9H_5ClN_2O_7S$. Calculated (%): C, 33.71; H, 1.57; Cl, 11.06; N, 8.74; S, 10.00.

4-(2-Methyl-4,6-dinitrobenzo[*b*]furan-3-ylsulfonyl)morpholine (6). Morpholine (4 mL, 4.6 mmol) was added to compound **5** (0.73 g, 2.3 mmol) in stirred acetonitrile (5 mL). The reaction mixture was kept for 1.5 h. The precipitate that formed was filtered off and recrystallized from a minimum amount of acetonitrile. The yield was 66%, m.p. 221—223 °C. Found (%): C, 42.21; H, 3.42; N, 11.01. $C_{13}H_{13}N_3O_8S$. Calculated (%): C, 42.05; H, 3.53; N, 11.32. ^{1}H NMR (DMSO-d_6), δ: 3.10—3.20, 3.60—3.70 (both m, 4 H each); 8.85, 9.00 (both s, 1 H each).

2-(2-Dimethylaminoethenyl)-4,6-dinitrobenzo[*b*]furan (7). A mixture of 2-methyl-4,6-dinitrobenzo[*b*]furan (**2a**) (0.51 g, 2.3 mmol) and dimethylformamide dimethyl acetal (4 mL) was refluxed for 2.5 h (monitoring by TLC with $CHCl_3$ as an eluent). The reaction mixture was cooled, diluted with light petroleum, and filtered. The yield was 80%, m.p. 152—154 °C. Found (%): C, 52.31; H, 3.74; N, 15.37. $C_{12}H_{11}N_3O_5$. Calculated (%): C, 51.99; H, 4.00; N, 15.16. ^{1}H NMR (DMSO-d_6), δ: 3.10 (s, 6 H); 5.40 (d, 1 H, ^3J = 16.1 Hz); 7.00 (s, 1 H); 7.90 (d, 1 H, ^3J = 16.1 Hz); 8.30, 8.73 (both s, 1 H each).

Synthesis of *O*-(3-amino-5-nitrophenyl) ketoximes 9a—e (general procedure). Hydrazine hydrate (10 mL, 0.2 mol) was added to a mixture of an appropriate *O*-(3,5-dinitrophenyl) ketoxime **1** (0.1 mol), $FeCl_3 \cdot 6H_2O$ (0.13 g, 0.5 mmol), and activated carbon (6 g) in methanol (700 mL). The reaction mixture was refluxed until the starting dinitro compound was completely consumed (monitoring by TLC with $CHCl_3$ as an eluent) and filtered hot. The carbon was washed with hot methanol (2×50 mL), the filtrate was cooled to 4 °C, and the precipitate that formed was filtered off.

***O*-(3-Amino-5-nitrophenyl)-1-phenylethanone oxime (9a).** Reaction time 3 h, yield 72%, m.p. 157—159 °C. Found (%): C, 62.12; H, 4.95; N, 15.84. $C_{14}H_{13}N_3O_3$. Calculated (%): C, 61.99; H, 4.83; N, 15.49. ^{1}H NMR (DMSO-d_6), δ: 2.45 (s, 3 H); 5.92 (s, 2 H); 6.92 (s, 1 H); 7.10—7.22 (m, 2 H); 7.45—7.55 (m, 3 H); 7.76—7.90 (m, 2 H).

***O*-(3-Amino-5-nitrophenyl)-1-(4-chlorophenyl)ethanone oxime (9b).** Reaction time 7 h, yield 60%, m.p. 155—157 °C. Found (%): C, 54.65; H, 3.59; Cl, 11.72; N, 13.58. $C_{14}H_{12}ClN_3O_3$. Calculated (%): C, 55.00; H, 3.96; Cl, 11.60; N, 13.74. ^{1}H NMR (DMSO-d_6), δ: 2.43 (s, 3 H); 5.91 (s, 2 H); 6.89 (s, 1 H); 7.10—7.18 (m, 2 H); 7.55, 7.65 (both d, 2 H each, ^3J = 8.0 Hz).

***O*-(3-Amino-5-nitrophenyl)-1-(2-chlorophenyl)ethanone oxime (9c).** Reaction time 8 h, yield 50%, m.p. 136—138 °C. Found (%): C, 54.78; H, 3.98; Cl, 11.24; N, 13.62. $C_{14}H_{12}ClN_3O_3$. Calculated (%): C, 55.00; H, 3.96; Cl, 11.60; N, 13.74. ^{1}H NMR (DMSO-d_6), δ: 2.45 (s, 3 H); 5.91 (s, 2 H); 6.85 (s, 1 H); 7.08—7.15 (m, 2 H); 7.46—7.64 (m, 4 H).

***O*-(3-Amino-5-nitrophenyl)-1-(2-methoxyphenyl)ethanone oxime (9d).** Reaction time 7 h, yield 71%, m.p. 146—147 °C. Found (%): C, 59.97; H, 5.12; N, 13.47. $C_{15}H_{15}N_3O_4$. Calculated (%): C, 59.79; H, 5.02; N, 13.95. ^{1}H NMR (DMSO-d_6), δ: 2.32, 3.83 (both s, 3 H each); 5.88 (s, 2 H); 6.82 (s, 1 H); 6.95—7.18 (m, 4 H); 7.30—7.55 (m, 2 H).

***O*-(3-Amino-5-nitrophenyl)-1-phenylpropan-1-one oxime (9e).** Reaction time 3 h, yield 68%, m.p. 188—192 °C. Found (%): C, 63.45; H, 5.49; N, 14.26. $C_{15}H_{15}N_3O_3$. Calculated (%): C, 63.15; H, 5.30; N, 14.73. ^{1}H NMR (DMSO-d_6), δ: 1.15 (t, 3 H, ^3J = 7.0 Hz); 2.92 (q, 2 H, ^3J = 7.0 Hz); 5.92 (s, 2 H); 6.91 (s, 1 H); 7.10—7.16 (m, 2 H); 7.45—7.56 (m, 3 H); 7.71—7.87 (m, 2 H).

Synthesis of 6-amino-4-nitrobenzofurans 8a—e and 4-hydroxy-6-nitroindoles 10a—e (general procedure). An appropriate *O*-(3-amino-5-nitrophenyl) oxime **9** (0.01 mol) was added to a mixture of ethanol (10 mL) and 36% HCl (10 mL). The reaction mixture was refluxed until the starting aminonitro compound was completely consumed (monitoring by TLC with $CHCl_3$ as an eluent). On cooling to ~20 °C, the precipitate that formed was filtered off and neutralized in water (50 mL) with aqueous ammonia to weakly basic reaction. The precipitate of 6-amino-4-nitrobenzofuran **8** was filtered off and dried *in vacuo*. The filtrate was evaporated to dryness and the residue was neutralized in water (50 mL) with aqueous ammonia to weakly basic reaction. The precipitate of 4-hydroxy-6-nitroindole **10** was filtered off, recrystallized from a minimum amount of ethanol, and dried *in vacuo*.

6-Amino-4-nitro-2-phenylbenzo[*b*]furan (8a). Reaction time 2 h, yield 38%, m.p. 192—194 °C. Found (%): C, 66.03; H, 3.95; N, 11.29. $C_{14}H_{10}N_2O_3$. Calculated (%): C, 66.14; H, 3.94; N, 11.02. ^{1}H NMR (DMSO-d_6), δ: 5.88 (s, 2 H); 7.18 (s, 1 H); 7.32—7.61 (m, 4 H); 7.68 (s, 1 H); 7.75—8.11 (m, 2 H).

4-Hydroxy-6-nitro-2-phenylindole (10a). Reaction time 2 h, yield 24%, m.p. 183—185 °C. Found (%): C, 66.20; H, 3.83; N, 10.96. $C_{14}H_{10}N_2O_3$. Calculated (%): C, 66.14; H, 3.94; N, 11.02. ^{1}H NMR (DMSO-d_6), δ: 7.10, 7.22 (both s, 1 H each); 7.31—7.42 (m, 1 H); 7.45—7.58 (m, 2 H); 7.75—8.00 (m, 3 H); 10.40, 12.15 (both s, 1 H each).

6-Amino-2-(4-chlorophenyl)-4-nitrobenzo[*b*]furan (8b). Reaction time 3 h, yield 31%, m.p. 278—280 °C. Found (%): C, 57.67; H, 4.17; Cl, 12.13; N, 9.62. $C_{14}H_9ClN_2O_3$. Calculated (%): C, 57.63; H, 4.12; Cl, 12.17; N, 9.61. ^{1}H NMR (DMSO-d_6), δ: 5.90 (s, 2 H); 7.15 (s, 1 H); 7.45—7.60 (m, 3 H); 7.68 (s, 1 H); 7.89 (d, 2 H, ^3J = 8.0 Hz).

2-(4-Chlorophenyl)-4-hydroxy-6-nitroindole (10b). Reaction time 3 h, yield 36%, m.p. 232—234 °C. Found (%): C, 57.55; H, 4.11; Cl, 12.22; N, 9.62. $C_{14}H_9ClN_2O_3$. Calculated (%): C, 57.63; H, 4.12; Cl, 12.17; N, 9.61. ^{1}H NMR (DMSO-d_6), δ: 7.10, 7.27 (both s, 1 H each); 7.58 (d, 2 H, ^3J = 8.0 Hz); 7.86 (s, 1 H); 7.92 (d, 2 H, ^3J = 8.0 Hz); 10.49, 12.32 (both s, 1 H each).

6-Amino-2-(2-chlorophenyl)-4-nitrobenzo[*b*]furan (8c). Reaction time 2 h, yield 27%, m.p. 178—182 °C. Found (%): C, 57.54; H, 4.18; N, 9.62. $C_{14}H_9ClN_2O_3$. Calculated (%):

C, 57.63; H, 4.12; N, 9.61. ^{1}H NMR (DMSO-d_6), δ: 6.00 (s, 2 H); 7.09, 7.21, 7.29 (all s, 1 H each); 7.45—7.56 (m, 3 H); 7.52—7.59 (m, 1 H).

2-(2-Chlorophenyl)-4-hydroxy-6-nitroindole (10c). Reaction time 2 h, yield 21%, m.p. 226—228 °C. Found (%): C, 57.71; H, 4.04; N, 9.63. $C_{14}H_9ClN_2O_3$. Calculated (%): C, 57.63; H, 4.12; N, 9.61. ^{1}H NMR (DMSO-d_6), δ: 7.06, 7.29 (both d, 1 H each, ^4J = 1.8 Hz); 7.51—7.60 (m, 2 H); 7.65, 7.85 (both dd, 1 H each, ^3J = 7.9 Hz, ^4J = 2.0 Hz); 7.91 (d, 1 H); 10.40, 12.15 (both s, 1 H each).

6-Amino-2-(2-methoxyphenyl)-4-nitrobenzo[*b*]furan (8d). Reaction time 2 h, yield 36%, m.p. 212—214 °C. Found (%): C, 63.35; H, 4.26; N, 9.88. $C_{15}H_{12}N_2O_4$. Calculated (%): C, 63.38; H, 4.23; N, 9.85. ^{1}H NMR (DMSO-d_6), δ: 4.00 (s, 3 H); 5.58 (s, 2 H); 7.09 (t, 1 H, ^3J = 8.0 Hz); 7.15—7.27 (m, 2 H); 7.41 (t, 1 H, ^3J = 8.0 Hz); 7.52, 7.64 (both s, 1 H each); 7.90 (d, 1 H, ^3J = 8.0 Hz).

4-Hydroxy-2-(2-methoxyphenyl)-6-nitroindole (10d). Reaction time 2 h, yield 21%, m.p. 252—254 °C. Found (%): C, 63.42; H, 4.19; N, 9.90. $C_{15}H_{12}N_2O_4$. Calculated (%): C, 63.38; H, 4.23; N, 9.85. ^{1}H NMR (DMSO-d_6), δ: 3.97 (s, 3 H); 7.02—7.25 (m, 4 H); 7.30—7.47, 7.78—7.88 (both m, 1 H each); 7.98, 10.32, 11.79 (all s, 1 H each).

6-Amino-3-methyl-4-nitro-2-phenylbenzo[*b*]furan (8e). Reaction time 4 h, yield 29%, m.p. 149—150 °C. Found (%): C, 66.87; H, 4.25; N, 10.77. $C_{15}H_{12}N_2O_3$. Calculated (%): C, 67.16; H, 4.48; N, 10.45. ^{1}H NMR (DMSO-d_6), δ: 2.32 (s, 3 H); 5.82 (s, 2 H); 7.08, 7.38 (both s, 1 H each); 7.39—7.59 (m, 3 H); 7.65—7.76 (m, 2 H).

4-Hydroxy-3-methyl-6-nitro-2-phenylindole (10e). Reaction time 4 h, yield 37%, m.p. 139—140 °C. Found (%): C, 67.55; H, 4.40; N, 10.47. $C_{15}H_{12}N_2O_3$. Calculated (%): C, 67.16; H, 4.48; N, 10.45. ^{1}H NMR (DMSO-d_6), δ: 2.60 (s, 3 H); 7.25 (s, 1 H); 7.38—7.46, 7.51—7.58, 7.65—7.71 (all m, 2 H each); 10.37, 11.83 (both s, 1 H each).

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